Citation for published version:
Johns, M 2014, 'Predicting the Solubility of Cellulose in Organic Electrolyte Solutions', DTC Summer Showcase 2014, Bath, UK United Kingdom, 7/07/14 - 9/07/14.

Publication date:
2014

Document Version
Early version, also known as pre-print

Link to publication

University of Bath

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Download date: 05. May. 2023

Predicting the Solubility of Cellulose in Organic Electrolyte Solutions

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1. Introduction

The material properties and abundance of cellulose mean that it has the potential for use as a biomaterial in tissue engineering.[1] However, the current commercial processes for its dissolution are not ideal for *in vivo* applications given the use of heavy metals and oxidising agents.[2] A 'greener', more efficient process compared to these has been reported using ionic liquids.[1,2] Rinaldi reported that the addition of a polar aprotic co-solvent to create an organic electrolyte solution, OES, reduced viscosity of the solution and enabled the instantaneous dissolution of cellulose.[3] In order to optimise this process it would be ideal to be able to predict the solubility of cellulose under different conditions and choices of ionic liquid/co-solvent that minimise potential toxic effects. This model is an initial attempt to achieve this by being able to predict the solubility of microcrystalline cellulose in solutions of 1-ethyl-3-methylimidazolium acetate, EMIm[AcO], and various co-solvents at 70 °C.

2. Co-Solvent Parameters

Solvent	Kamlet-Taft Parameters				Gutmann Numbers		
	$E_T(30)$	π*	β	$E_T(30)/β$	AN	DN	Difference
1,3-dimethyl-2-imidazolidinone	42.4	0.92	0.79	53.67	15.7♦	27.8	12.1
tetramethylurea	41	0.83	0.8	51.25	9.2	31	21.8
diethyl carbonate	37	0.45	0.4	92.50	6♦	16.4	10.4
dibutyl ether	33	0.27	0.46	71.74	3.9	19.2	15.3
dimethyl acetamide	43.7	0.88	0.76	57.50	13.6	27.8	14.2
1-methyl-pyrrolidin-2-one	42.2	0.92	0.77	54.81	13.3	27.3	14
tetrahydrofyran	37.4	0.58	0.55	68.00	8	20	12
dimethyl formamide	43.8	0.88	0.69	63.48	16	26.6	10.6
dimethyl sulfoxide	45.1	1.00	0.76	59.34	19.3	29.8	10.5
dimethoxyethane	38.2	0.53	0.41	93.17	10.2	20	9.8
ethyl acetate	38.1	0.55	0.45	84.67	9.3	17.1	7.8
dioxane	36	0.55	0.37	97.30	10.3	14.3	4
γ-valerolactone	46.9■	0.83	0.6	78.17	13.8♦	23.4♦	9.6
propylene carbonate	47.2	0.83	0.4	118.0	18.3	15.1	-3.2
benzonitrile	41.5	0.9	0.37	112.2	15.5	11.9	-3.6
sulfolane	44	0.98	0.39	112.8	19.2	14.8	-4.4
acetonitrile	45.6	0.75	0.4	114	18.9	14.1	-4.8
1-methylimidazole	44.6	1.03	0.73	61.10	21.2♦	28.5♦	7.3

The Kamlet-Taft solvatochromatic relationship is a series of empirical values that allow the separate measurement of the polarity, $E_T(30)$; hydrogen bond donor, α; hydrogen bond acceptor, β, and polarisability, π*, properties of solvents.[4]

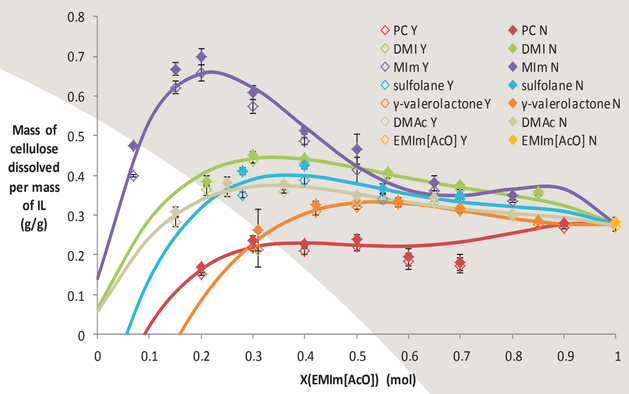
The Gutmann Numbers are empirical values that are measures of the relative strength of solvents as Lewis acids or bases. These are the acceptor number, AN, and the donor number, DN.[5]

■ Predicted using the equation $E_T(30) = -(E_T(33) - 64.622799092) / 0.2490147546$

♦ Predicted using the equation $AN = -3.29 + 20.6π^*$

♦ Predicted using the equation $DN = -0.19 + 39.23β$

3. Model Development



Predicted curves and experimental data

Constants for co-solvents with $E_T(30)/β < 65$

Solvent Specific Parameter	Universal Constants		
	i	ii	iii
a	0.118650946	-50.945377	48.93405447
b	-0.24969509	114.2427472	-109.2104501
c	0.233831713	-83.90772271	75.30967119
d	-0.099378569	20.17523923	-14.44001628
e	-0.001019406	0.476937045	-0.419561222

Constants for co-solvents with $E_T(30)/β > 65$

Solvent Specific Parameter	Universal Constants		
	i	ii	iii
a	-0.158199978	-3.564080286	15.35794294
b	0.294422578	10.53577771	-29.17860458
c	-0.102601579	-11.96342717	12.38109763
d	-0.029014733	4.791450889	2.6564779
e	-0.000158239	0.283325787	-1.21947885

- The model is based on 3 of the 4 Kamlet-Taft Parameters - $E_T(30)$, π* and β. α is 0 for all aprotic solvents so was not included
- Cellulose dissolution experiments, carried out by Remigius Wirawan, were carried out for 6 co-solvents. Average values obtained for the concentration of cellulose at which complete dissolution was achieved, Y, and incomplete dissolution was achieved, N, at varying concentrations of EMIm[AcO]. The 6 co-solvents were 1-methylimidazole, MIm; 1,3-dimethyl-2-imidazolidinone, DMI; dimethyl acetamide, DMAc; propylene carbonate, PC; sulfolane, and γ-valerolactone
- A 4th degree polynomial curve was fitted to each solvent data set:

$$y = a_{co\text{-}solvent}x^4 + b_{co\text{-}solvent}x^3 + c_{co\text{-}solvent}x^2 + d_{co\text{-}solvent}x + e_{co\text{-}solvent}$$

- Constants such that the sum of the 3 Kamlet Taft parameters, each multiplied by a universal constant, for each co-solvent equalled the co-solvent specific values for the polynomial equation:

$$n_{co\text{-}solvent} = i_n E_T(30)_{co\text{-}solvent} + ii_n π^*_{co\text{-}solvent} + iii_n β_{co\text{-}solvent}$$

Where: $n_{co\text{-}solvent}$ = a, b….e for a specific co-solvent

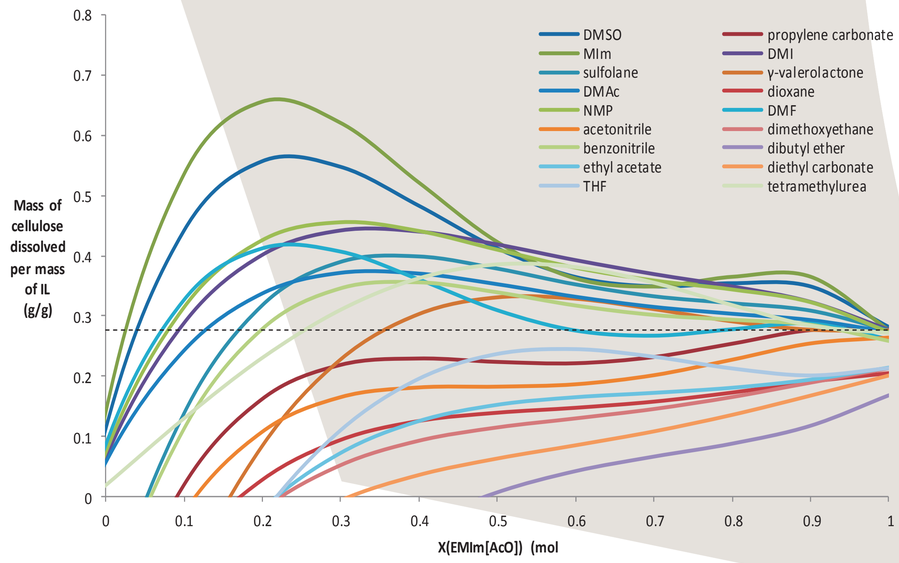
i_n, ii_n, iii_n = universal constants for a, b….e

$E_T(30)_{co\text{-}solvent}$, $π^*_{co\text{-}solvent}$, $β_{co\text{-}solvent}$ = Kamlet-Taft Parameters for specific co-solvent

- Solvents divided into 2 categories dependent on the ratio between $E_T(30)$ and β

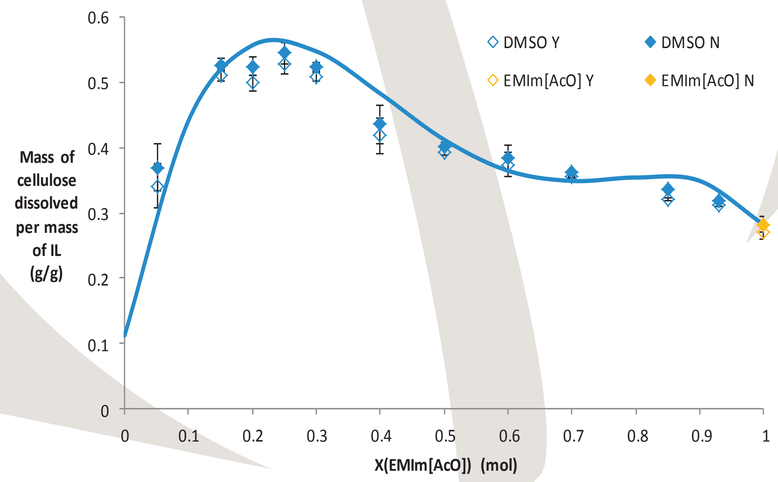
4. Predicted Cellulose Solubility

Not all solvents enhance the solubility of cellulose in ionic liquids. It is apparent that that the ratio between $E_T(30)$ and β plays an important role in this with solvents with high ratios between the two being less effective.



Predicted cellulose solubility curves, dashed line is cellulose solubility in pure EMIm[AcO]

5. Confirmation of the Model



Predicted curve for DMSO and experimental data

- DMSO chosen as co-solvent to be tested given that Rinaldi reported it having the lowest concentration of ionic liquid required in order to achieve instantaneous dissolution[3]
- Experimental values obtained by R. Wirawan
- Predicted dissolution curve fits data from experiments well

6. Conclusions & Future Work

A model predicting the solubility of microcrystalline cellulose in organic electrolyte solutions comprising of EMIm[AcO] and a polar aprotic co-solvent at 70 °C was developed. The model highlights the importance of the ratio between $E_T(30)$ and β for the co-solvent and suggests that polar aprotic Lewis acids and bases may interact with the ionic liquid differently. Development of the model to take into account the dissolution temperature, the ionic liquid used and the degree of polymerisation of the cellulose would be beneficial, enabling the prediction of optimal solvent systems that can be used to create scaffolds for *in vivo* use, part of the future work with Ram Sharma.

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